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ELECTRICAL CHARGES IN LAYER-LATTICE SILICATES IN RELATION TO IONIC EXCHANGE

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ABSTRACT. Many layer-lattice silicates, *e.g.*, the micas and the clay minerals, show, especially in finely divided states, a marked capacity to exchange some of the exposed ions of the silicate lattice for similarly charged ions of a 'contact' solution. The mechanism of this ionic exchange and in particular, the nature and the origin of the (surface) charges which hold the exchangeable ions in the liquid phase at some distance from the surfaces of the crystallites has been discussed. The weakness of a purely colloidchemical explanation of these charges in terms of what are known as 'primarily absorbed ions' on the surface has been pointed out and our existing knowledge of the atomic structures of these crystals has been shown to provide a more real and reliable basis for discussions on the exchange reaction and the surface charge. The most polar ions (and, in some cases, groups) on the surface of the crystallites interact with the dipoles of the 'contact' liquid which makes them execute a certain type of oscillatory motion about mean positions in the liquid phase at some distance from the surface, and it is these ions which under suitable conditions, are exchanged for similarly charged ions present in the liquid phase. The mechanism of this ion-dipole interaction and its electrochemical consequences, especially, in regard to the exchange behaviour of the crystallites have been discussed, taking the mica-water system as a model The nature of the so-called 'broken bonds' developed on the lateral surfaces of the caystals and the role frequently attributed to them in determining the ion-exchange properties of these systems has also been discusssd The acidic and basic character of hydroxyl groups present in these silicates has been examined.

Many crystalline silicates, *e.g.*, the clay minerals and the micas, have a layer-lattice structure (Pauling, 1930). The characteristic structural element is a hexagonal network of O^{-2} ions co-ordinated tetrahedrally about Si^{+4} or Al^{+3} (Fig. 1). This network is joined through the unshared oxygen

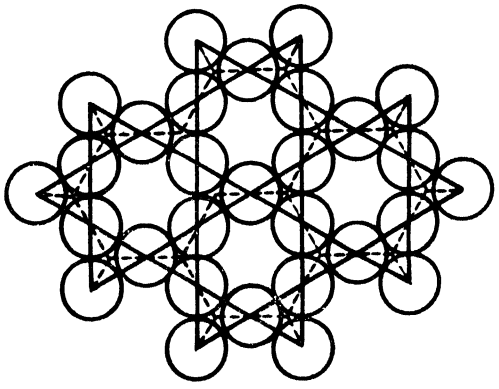

FIG. 1

Hexagonal network of linked Si(orAl)-O tetrahedra in which all the tetrahedra point in the same direction.

of each tetrahedral unit to groups of O^{-2} and OH^{-1} ions arranged octahedrally around ions like Al^{+3}, Mg^{+2} and Li^{+1}. Fusion of the tetrahedral and octahedral layers gives the unsymmetrical packet, $Al_2Si_2O_5(OH)_4$ (Fig.2*a*), found in clay minerals of the kaolin group. A symmetrical packet having the composition $Al_2Si_4O_{10}(OH)_2$ (Fig. 2*b*) is formed when a second tetrahedral layer is attached to the octahedral sheet from the other side and it occurs in the mineral pyrophyllite and, with some ismorphous replacement of the Si and/or Al by cations having a smaller positive charge, in the micas and clay minerals of the montmorilionite and illite groups. Both the 2-layer and the 3-layer silicates can and do take up cations (or bases) from solutions in exchange for cations already present in the silicate lattice. Anions, as a rule, do not have much preference and even when taken up are much less eagerly retained. Exception is made in the case of certain anions the most important of which is PO^{-3}_4.

The fact that the silicate crystal can take up cations and anions from solutions shows that it contains potentially active negative and positive centres

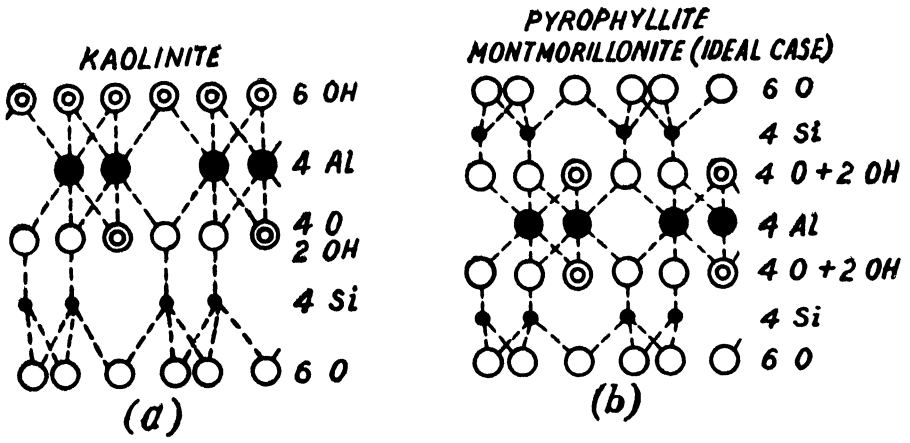

FIG. 2

in the lattice. Clay crystallographers believe that the exchangeable ions of clays are constituents of the silicate lattice being held opposite such potential centres of charges and yet accessible to the ions of a contact solution (Hendricks, 1945). The existence of these 'charge centres' is also indicated by the electro-kinetic behaviour of clays in ionising media. Depending on its own constitution and its ionic environment in the medium, the clay crystal migrates towards one of the electrodes at a definite rate, the exchangeable ions—they are the *gegenions* or counter ions of Pauli, moving towards the opposite electrode.* In a stable

* A simultaneous discharge of cations as well as anions takes place when aqueous suspensions of the clays are electrodialysed. The clay appears to suffer a hydrolytic cleavage, the H^+ and OH^- of water taking the places of the cation and the anion respectively.

suspension of the clay in an ionising solvent, the exchangeable ions, like all other counter ions, show quite definite and measurable conductivity and activity co-efficients (Wiegner and Pallmann, 1929; Mitra, 1936, 1940, Marshall., 1942,) properties which are, however, lacking in the clear ultrafiltrate of the sol (Mitra, *loc. cit.*). The existence of charge centres on the surface of the clay crystal which hold the exchangeable ions in the liquid phase at some distance from the surface is thus beyond doubt. But how do these (surface) charges come about? According to the well-known theory of Mukherjee (1920-21) and Fajans (1921) one would refer these charges to a primary adsorption (*i.e.*, adsorption by chemical or valence forces) of ions on the surface of the clay particles. Mukherjee and his co-workers (1933, 1937, 1945) have used this theory to great advantage in their discussions on the electrical properties of colloids including hydrosols of hydrogen (or, acid) clays. While the merits of the adsorption theory as a convenient working hypothesis for purposes of qualitative discussions on several aspects are beyond question, its limitations become obvious coming down to details and individual systems. For instance, identification of the 'primarily adsorbed' ions is far from easy in most cases, and the difficulty becomes almost insurmountable when one has to deal with endless sheets of co-ordinated ions as obtain in the clay minerals and other layer-lattice silicates. Fortunately, our knowledge of ion lattices in general and of the lattice-structure of platy silicates including the clays in particular, has developed to an extent as would make it unnecessary to invoke any adsorption hypothesis to account for the surface charges in these silicate crystals. Taking, for instance, the muscovite structure which is now so well understood mainly from the work of Jackson and West (1931) the K-ions in the interior of the lattice are known to be co-ordinated by electrostatic bonds to twelve O^{-2} ions (Fig.3) and yet these same K ions are readily exchanged when brought to the surface by cleavages

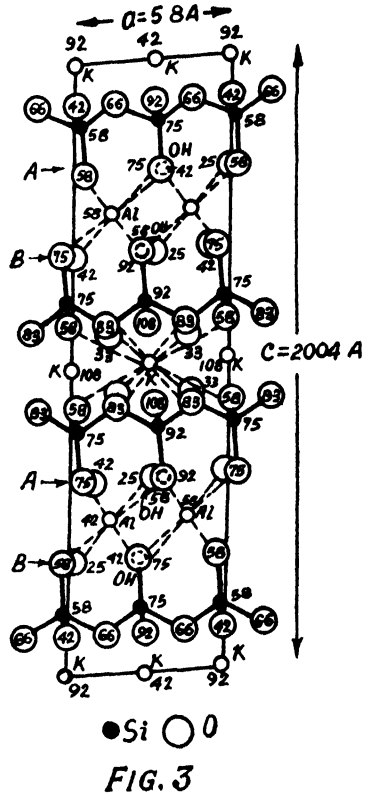

FIG. 3

The structure of Muscovite projected on (010) (After Jackson and West).

The heights of the atoms above the face of the unit cells, as measured along the axis of projection, are indicated by the numbers An atom on the lower face of the unit cell is indicated by 0, on the top face by 100, and intermediate heights are given accordingly.

of the crystal perpendicular to the *c*-axis.* Each exposed K ion will now be co-ordinated to six oxygen ions if the cleavage has been perfect and it would be unnecessary to take recourse to any adsorption mechanism to account for the presence of the K^+ ions on the surface. The crystal chemist can probe deeper into the crystal and find a reason for the bonding (or co ordinating) power of the oxygens for the potassiums. He can trace this bonding power to unsatisfied oxygen valencies arising from a tetrahedral co-ordination of the oxygen ions around Al^{+3}'s in addition to the Si^{+4}'s, one in every four silicons having been replaced isomorphously by an Al^{+3}. Cations in the octahedral layer may similarly be replaced by others having a smaller positive charge—Mg^{+2} for Al^{+3} is the major replacement in the montmorillonites (Marshall, 1935) and the crystal chemist has been able to offer a very plausible explanation of the negative charges within the lattice on the basis of such replacements. The exchangeable cations only serve to balance these negative charges. Very fair agreement between the observed cation exchange power of montmorillonite and that calculated from isomorphous replacements has been obtained (Nagelschmidt, 1935, Marshall, *loc. cit.*). The balancing cations in this mineral can be exchanged for large organic cations (Giesecking, 1939, Nelson and Hendricks, 1943). Different organic cations have been found to give different values of the basal spacing (001) which, combined with a knowledge of the sizes of the organic cations, definitely shows that the balancing (or exchangeable) cations in montmorillonite are held between the three-layer packets in much the same manner as the potassiums in muscovite.

While the above explanation of the negative charges seems to work quite well for most layer-lattice silicates having the 2:1 or symmetrical lattice!, it breaks down in the case of the 1:1 or unsymmetrical silicates, *e.g.*, kaolinite where isomorphous replacement is rather the exception than the rule, and the two-layer packets are practically neutral being made up in most cases almost exclusively of Si-O tetrahedra and Al (or Mg)−O(or OH) octahedra. There are no multi-co-ordinated large metal cations in the lattice (required for balancing negative charges arising from isomorphous replacements) which can be exchanged for those of an added electrolyte and yet finely ground kaolinite has been reported to take up cations from solutions to the extent of 100.5 milliequivalents per 100 gms. of the solid (Kelley and Jenny, 1936). To what is this cation binding power due? One answer to this question, which has been frequently given, is that the cations are held on the lateral surfaces of the sheets where unsatisfied negative charges or valencies are developed as a result of lattice termination (Hendricks, *loc. cit.*). The lateral surface increases on grinding which produces fractures

* Tetrahedral Al^{+3} being absent in the analogous platy mineral pyrophyllite, $Al_2Si_4O_{10}(OH)_2$, there are no unsatisfied oxygen valencies to hold multi-co-ordinated large cations such as K^+ which become exchangeable on being brought to the surface by cleavages perpendicular to the *c*-axis.

Chief exceptions are pyrophyllite and talc.

parallel to the *c*-axis by breaking valence bonds between Si and O, and between Al and O (or, OH). The fact that the cation binding power of kaolinite increases on grinding (Kelley and Jenny, *loc. cit.*) is, on this theory, to be attributed to an increase in the number of the broken bonds. This explanation has been critically examined in a recently published paper (Mitra, 1946) where it has been pointed out that if a cation's combining power is at all to be attributed to the broken bonds, an anion's binding capacity due to the same cause has to be simultaneously recognised, *i.e.*, the mineral must be considered amphoteric and not merely acidic. This follows directly from the "principle of microscopic neutrality" which requires that potentially positive and negative ends or poles be produced simultaneously and in equivalent numbers by the rupture of the ionic bonds. The finely ground solid would therefore tend to take up equivalent amounts of cations and anions from a contact-solution and not merely cations. Failure to appreciate this fundamental aspect of the broken ionic bond has been responsible for much of the confusion which exists in discussions of the relationship of the cation exchange capacity of clays to their crystal structure. One might refer in this connection to the criticism made by Kelley and Jenny (*loc. cit.* against a suggestion of Hofmann, Endell and Wilm (1934) according to which the exchangeable cations in clays are held by broken bonds on the edges of the Si-O planes. Kelley and Jenny ask, "If the broken bonds should bind cations from the solution, what would happen to the remaining anions in solution?" They argue that "if their (Hofmann *et al's*) hypothesis is valid, then when the clay fragments were removed from the solution more anions than cations would be left in the solution but such a system cannot exist, for it violates the law of electro-neutrality." They realise that "a solid cannot adsorb cations from solutions without an exchange process or an equivalent adsorption of anions" but fail to see that in the broken bond a cause for an equivalent adsorption of anions exists just as surely—theoretically at least—and for the same reason as it does for an adsorption of the cations. The 'broken bond theory' may or may not be true but the argument which Kelley and Jenny use to reject it is not quite convincing. Their criticism would be certainly valid if only a cation's binding power were attributed to the broken bonds as, indeed, appears to have been done by Hofmann *et al* and, more recently, by Hendricks (*loc. cit.*). Actually, however, the broken bonds would tend to bind—it is not claimed that they will actually do so—both cations and anions, *i.e.*, they would give a potentially amphoteric character to the comminuted solid—an aspect to which no reference is found in the writings of the above investigators

Let us now examine the more fundamental question: Is the broken bond theory at all plausible, that is, will the broken bonds in clay crystals and, for the matter of that, in any insoluble ionic crystal at all remove cations and anions from a contact solution? We might also put the question like this: will the act of comminution at all give rise to positive and negative

ends or poles which can exert sufficiently strong resultant positive and negative electrical fields external to the crystal so as to be able to remove cations and anions from a contact solution by electrostatic attraction? The strengths and separations of the oppositely charged poles appear to be the most important factors which have to be considered for answering this question. This is, of course, true in so far as the ionic wall is concerned. Factors like the size, valency, polarisability and state of hydration of the ions of the contact solution would also matter but not unless there are strong enough electrostatic fields beyond the crystal surface. We believe that with most ionic crystals made up of closely packed oppositely charged ions, the odds will be very much against the spacings between the positive and negative poles being large enough to admit of the creation of sufficiently strong negative and positive electrical fields external to the crystal which can attract cations and anions from a contact solution and fix them to the solid wall. It must be remembered that of the poles developed by comminution, contiguous ones will carry dissimilar rather than similar charges in a statistical sense. Let us take the case of the endless sheet of linked Si-O tetrahedra. In breaking this sheet numerous Si-O-Si bonds will be ruptured. When any two linked tetrahedra are torn apart, the oxygen through which they were linked can evidently go with only one of the silicons giving it a nett negative charge, a positive charge being left with the other silicon. Suppose, now, a circular disc is taken out from the sheet and we then fix our attention on the peripheral silicons of this disc (Fig. 4). We shall find that if a particular Si has been forced to part with one of its linked oxygens (*e.g.*, the oxygen marked 1) in favour of the other part of the sheet giving a silicon-oxygen configuration having the composition ($SiO_{3/2}$) and carrying one unit of positive charge, then the silicon on the disc contiguous to it will have completely appropriated to itself an oxygen ion (the oxygen marked 2 in the figure) which has been torn off the other part of the sheet giving an Si-O

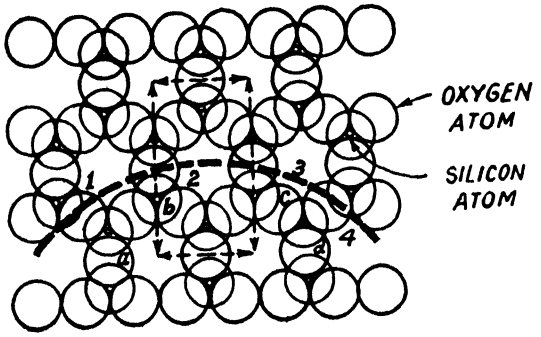

FIG. 4

assemblage with the composition ($SiO_{3/2}$) and carrying one extra unit of negative charge. This is a physical necessity in as much as the positive charge gained by the Si which has lost one linked oxygen will, by electros-

tatic attraction, try to win for the contiguous Si a complete oxygen ion taken from the other part of the sheet so that the positive charge may be balanced. The ionic crystal must be, to put it in Hendricks' language, "statistically neutral *on the smallest possible scale*" (Hendricks, 1945, *loc. cit.*). This should be so for the surface just as well as for the interior. The sheet can break only according to this plan. The act of comminution cannot chalk out an atomic line of demarcation just anyhow and anywhere through the sheet. The question, now, is, will the two peripheral contiguous $(SiO_4/_2)^{+1}$ and $(SiO_5/_2)^{-1}$ groups act as discrete centres of positive and negative charges towards the anions and cations of a contact solution with forces strong enough to bind them to the solid wall? Or, will there be a spatial rearrangement of the oxygens around the peripheral silicons so as to annul any possible external effect of contiguously situated oppositely charged poles created by comminution? The odds, we believe, are in favour of the second possibility which, in effect, amounts to a mutual cancellation of the positive and negative fields of contiguous poles so as to inhibit, or, even completely destroy a possible amphoteric character of the solid wall giving a substance akin to the socalled "Aquivalenz Korper" of Fajans.

Hydroxyl groups in layer-lattice silicates are often considered as the principal ionogenic groups capable of giving rise to positive as well as negative charges by dissociating as OH groups or as H ions, the ionic composition of the medium, especially, its p_H, determining which type of dissociation will occur. According to Kelley and Jenny (*loc. cit.*), the acid character, *i.e.*, the cation exchange power of the minerals kaolinite and pyrophyllite is entirely due to the OH groups of the lattice. Kaolinite has two types of OH planes (Fig. 2,a), one made up entirely of OH groups and forming the exposed surface of a lattice packet and the other, a composite (O,OH) plane imbedded within a hexagonal network of oxygen ions. Only the subsurface OH groups are present in pyrophyllite (and other clay minerals having a 3-layer lattice). This difference would lead one to expect that hydrogen kaolinite should be dibasic Mitra, 1941-42), while a monobasic acid character is shown by pyrophyllite.† Hydrogen montmorillonite usually behaves as a monobasis acid (Mitra, Mukherjee and Mitra, (1946). Its acid character is due mainly to the H ions on the surface of the 3-layer packets derived from an exchange of the balancing cations of the lattice. Being at a considerable distance from the centres of negative charges which in montmorillonite are mainly located in the octahedral layer, these H ions are expected to be more dissociable than the hydrogens of the OH groups. The usually observed monobasic acid character of hydrogen montmorillonite is to be attributed to a neutralisation of these

* OH groups belonging to the subsurface (O, OH) plane are also accessible through the hexagonal rings in the superimposed oxygen network provided, of course, the incoming ion has a diameter smaller than that (3Å) of the hexagonal ring.

† Unpublished work of K. S. Rajagopalan

readily dissociable H ions. The expected second stage of dissociation due to the hydroxylic hydrogens, is perhaps too weak for detection (as in the case of the third stage of dissociation of phosphoric acid), a contributing factor being the tendency of the first stage of dissociation to suppress the second.

A polybasic acid character of the layer-lattice silicates might be expected on other grounds. These become evident when the different possible types of isomorphous replacements in the lattice are considered. Such replacements may occur in tetrahedral as well as octahedral layers. The separation of the negative charge from the H ions on the surface of the lattice packet will be different in the two cases and consequently the strength of the electrostatic bond holding them will also be different. The H ions will, therefore, have different energies of dissociation. The fact that hydrogen montmorillonite usually shows a monobasic acid character is consistent with the current notion that in montmorillonite isomorphous replacement is almost entirely confined to the octahedral layer. The characteristic replacement in the micas is of Al^{+3} for tetrahedral Si^{+4}. The seat of the negative charge is nearer to the surface than in montmorillonite and consequently mica should behave as a weaker acid than montmorillonite.* It would indeed be interesting from the point of view of the crystal chemistry of these silicates to follow up the electrochemical consequences of various types of isomorphous replacements expressed in terms of such features as the conductivity and activity coefficient of the gegenions, the nature of titration curves with bases and the magnitude of the free acid to the total neutralisable acid of hydrogen, or, acid systems. Investigations on these lines are being carried out in this laboratory.

A good case for the basic character of the planar OH groups in kaolinite seems to have been made on the basis of the interaction of this mineral with phosphoric acid, or, acid phosphates. This reaction is more and more favoured as the p_H of the phosphate solution diminishes and at a sufficiently low p_H, Stout (1939) found a complete replacement of the planar OH groups in finely ground kaolinite by PO_4^{-3} ions. The subsurface OH groups being not accessible to the large PO_4^{-3} ions through the hexagonal rings of oxygens were naturally left unreacted upon. The planar OH groups, however, are all accessible as their complete replacement indicates. But the kaolinite structure is such that an exposure of all the planar OH groups necessarily entails an opening up of all the subsurface OH groups of the lattice as well. These latter OH groups can react with such ions in solution as have a diameter smaller than the hexagonal rings of oxygens within which they are embedded. For example, they can react with the strong bases. Assuming then that the OH groups in kaolinite, planar as well as subsurface, have a potentially acid character, a high value of the cation binding power comparable to the phosphate fixing capacity would be expected in alkaline solutions. Actually, however, Stout's data indicate a much smaller cation binding power, the

* Unpublished work of K. S Rajagopalan appears to substantiate this view.

value 78.0 m e. per 100 gms., recorded at as high a p_H as 11.0, representing only about 5 0 per cent of the total amount (1,550 m e.) of OH groups in 100 gms. of the mineral.

One way out of the above inconsistencies would be to give up the idea that OH groups in kaolinite are responsible for its acid character. Other ways also exist. For instance, it might be argued that a complete replacement of the planar hydroxyl by PO_4^{-3} ions does not necessarily indicate that all of them had been lying exposed from the very beginning. The individual packets in kaolinite are held by fairly strong hydrogen bonds and the mineral, even when finely ground, would hardly be expected to give single-packet platelets. It is just possible, however, that with progressive intake of PO_4^{-3} ions, more and more OH groups open up and are made available to the action of the phosphate. This would no doubt happen if the phosphated kaolinite separated out as a second solid phase. Stout's observation (Stout, *loc cit.*), that finely ground kaolinite, when phosphated, becomes amorphous to X-rays, seems to support the assumption that a second solid phase is formed.

The same line of reasoning may be followed to see what happens when a strong acid like HCl reacts with kaolin. As before, hydroxyls will be replaced by Cl's, however, the Cl being a misfit in the crystal mainly because of a much larger diameter than OH, has to keep out of the solid kaolin phase. On the other hand, the lattice energy of $AlCl_3$ is not large enough to admit of the formation of a separate solid phase under the existing conditions. The Cl, therefore, remains in a diffusible, or, dissociated condition imparting a positive charge to the surface. This positive charge hampers the dissociation of further OH groups and may thus make inoperative even such amongst them as are lying on the exposed surfaces of the lattice packets. Remembering that a very large number of the OH groups are likely to be blocked within the multi-packet particles, it follows that a very small fraction of the kaolinitic OH's will react with the acid at moderate concentrations It is only at very high concentrations of the acid that the basic character of kaolinite will be expected to have its full play. Under these conditions, every Al^{+3} ion will have its full complement of 3 Cl^- ions and the kaolinite lattice will break up into $AlCl_3$ and silicic acid.

A similar state of affairs would be expected in the interaction of kaolin with an alkali. The neutralisation of some of the OH groups would give a greater negative charge to the surface* and make the dissociation (and neutralisation) of further OH groups difficult for this reason and since the sodium salt does not form a separate solid phase a much smaller number of OH groups will be attacked by the alkali than by phosphate ions in an acid medium as Stout's results definitely show In strongly alkaline solutions, however, the lattice will break up into sodium silicate and sodium aluminate.

* This follows from the fact that the sodium salt of a weak acid is more strongly dissociated than the acid itself.

The break-up of the lattice as a result of the dissolution of the reaction product, or, the formation of a second solid phase is an extreme case of the charging or discharging process associated with an ionic reaction of the silicate crystal. Of much greater interest are the milder reactions which leave the silicate lattice virtually intact and effect only an exchange of ions between the surface layers of the crystal and the liquid phase with a corresponding variation of the surface charge. Let us follow up such an ionic reaction of finely ground muscovite suspended in water. The K ions on the surface dissociate giving a nett negative charge to the platelets. A simple mechanism of the dissociation suggests itself. The K ions on the surface carry a residual positive charge being bonded to the solid phase by only six out of the required number of twelve oxygen ions. Being centres of positive charges, the surface potassiums orient and attract water dipoles with the negative polarities of the latter directed towards them and in doing so are themselves drawn by the dipoles towards the liquid side. The average amplitude of vibration of the surface K's will, for this reason, be greater than what it is in the body of the crystal and, in this sense, the K ions on the surface will exist partly in the liquid phase surrounded by water dipoles. They are not truly dissolved K-ions free to occupy any part of the liquid phase for as soon as they dissociate the surface gets a nett negative charge and the electrostatic attraction which is set up prevents a further outward journey of the K ions. Attention must here be drawn to one essential aspect. It must be clearly understood that when a muscovite crystal is split along the potassium-bearing plane the K ions distribute themselves equally between the two parts. On now directing our attention to the cleavage surface of *one of the platelets* (Fig. 5 *a*) we shall find that only a half of its exposed hexagonal rings of oxygens is occupied by K-ions and the other half is vacant. There will be an accumulation of 0.5 unit of (excess) positive

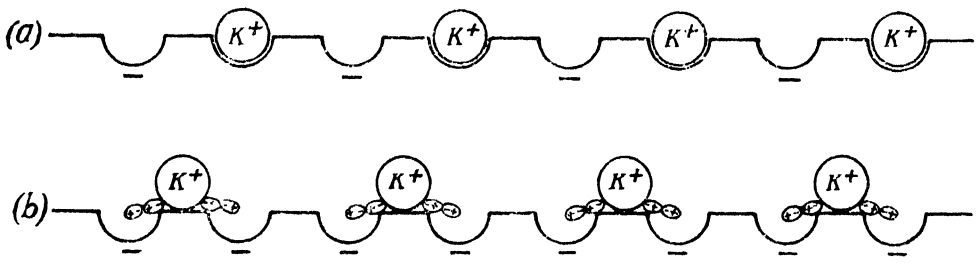

FIG. 5

charge in the region of an occupied ring while a vacant one will have 0.5 unit of negative charge focussed at its centre. The principle of microscopic neutrality will require that an occupied ring has as its immediate neighbour a vacant one in a statistical sense. In other words, positive and negative charges, each 0.5 unit in strength, will be distributed on the surface with

contiguous centres of charge carrying dissimilar charges. The muscovite crystal seeks to get rid of these local concentrations of opposite charges by interaction with the water dipoles in a manner such that the exposed potassiums are pulled out of their hexagonal cavities, or, rings and made to take up positions in between contiguously situated rings as roughly depicted in Fig. 5*b*. Such a redistribution of the surface potassiums following on their interaction with the water dipoles serves to make the surface statistically neutral on a smaller scale compared with the dry crystal, and to minimise the potential energy of the system—as it should in order that it may pass on to a stabler state of equilibrium. Each K-ion carrying one unit of positive charge now balances two 0.5 units of negative charge situated at the centres of adjacent hexagonal rings. Actually, the potassiums execute oscillations between these centres but taking the time average of this oscillatory motion, they may be looked upon as occupying mean positions between the centres as shown in Fig. 5*b*.

When a foreign electrolyte, *e.g.*, LiCl is added to such a system, the kinetic motion of the Li -ions will sometimes take them within the space between the negatively charged surface and the positively charged K'-ions. As positive charges cannot crowd together, the K -ions will be displaced (or exchanged) to pair with the diffusible anion, $Cl_,^-$ in the bulk of the liquid phase. The Li^+-ions which displace K'-ions become bonded to the surface by quite similar forces as their predecessors. Like the K's they will also register their activity on a reversible Li electrode. In the language of the colloid chemist, they are the mobile ions in a diffusible double layer. In the above discussion, however, hypotheses, inherent in a purely colloid chemical treatment, have been altogether circumvented. In particular, we have avoided invoking the primary adsorption of any anion to balance the positive charge of the dissociated K ions and give neutral "ion pairs" on the surface. The formulation of such ion pairs and their identification in individual systems constitude the very essence of the adsorption method of approach to problems relating to the electrochemistry of disperse systems. However, it would be unnecessary and even futile to try to single out such ion pairs in the case of the silicate crystal just as surely and for the same reason as it would be impossible to pick out neutral molecules in any ionic lattice, either in its interior or on the surface. Representation of these surface reactions in terms of primarily adsorbed ions and ion pairs on the surface may be sufficient for purposes of their qualitative discussion, but the basis of a quantitative theory can only be laid on a detailed knowledge of the structure of the crystallites, especially, of their surface layers. A complete quantitative theory will emerge only when in addition to this knowledge accurate information regarding the nature and the magnitude of the interaction between the ions on the surface of the crystallites, the ions of the contact solution and the molecules of the solvent is available.

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